

Claims:

An organic solvent-based printing ink composition which comprises
a cationic dyestuff of formula (1).

$$(R_6)_n \xrightarrow{R_2} R_3 \qquad (R_5)_m \qquad (1)$$

or a mixture thereof.

wherein R_1 - R_6 are independently of one another hydrogen, substituted or unsubstituted alkyl, alkoxy, cycloalkyl, aryl, heteroaryl or allyl, R_2 and R_3 may be combined together to form a ring, further R_5 and R_6 are independently of one another halogen, cyano, nitro, aryloxy, alkenyl, alkenoxy, alkoxcarbonyl, aryloxycarbonyl, acyloxy, acyl, alkylthio, arylthio, acylamino, alkylsulfonyl, arylsulfonyl or thiocyano, any two of R_5 or any two of R_6 may be combined together to form a homocyclic or heterocyclic aromatic or non-aromatic ring, m is an integer of 1 to 5, n is an integer of 1 to 4 and X^- is an organic anion,

- (2) an organic solvent,
- (3) an organic resin acid, or a salt thereof, soluble in the organic solvent, and
- (4) optionally a pigment.
- 2. The composition according to claim 1, wherein R_1 - R_6 in the dyestuffs of formula (1) are independently of one another hydrogen, unsubstituted or substituted alkyl or alkoxy of 1 to 10 carbon atoms, cycloalkyl of 5 to 10 carbon atoms, aryl of 6 to 10 carbon atoms, heteroaryl of 5 to 10 atoms, comprising one or more nitrogen, oxygen or sulfur atoms as ring members, or allyl, R_2 and R_3 may be combined together to form a 5 to 7-membered ring, and X^- , m and n have the meanings indicated.
- 3. A composition according to claim 2, wherein substituted alkyl comprises hydroxyalkyl, halogenoalkyl, aminoalkyl, cyanoalkyl or arylalkyl, substituted alkoxy comprises arylalkoxy, and aryl preferabyly comprises phenyl or naphthyl, optionally substituted by hyroxy-, halogeno-, amino-, cyano-, carboxy-, carbonamido-, sulfo- or sulfonamido.

- 4. The composition according to claim 2, wherein R_1 - R_4 are methyl, R_5 is methyl or methoxy (m is 1) or two R_5 together form -O-CH₂-O-CH₂-, R_6 is hydrogen and n is 1.
- 5. The composition according to any one of claims 1 to 4, wherein X^- is the anion of an organic acid, preferably a resin acid.
- 6. The composition according to claim 1, wherein the organic solvent (2) is selected from the group consisting of optionally halogenated aliphatic hydrocarbons, optionally halogenated aromatic hydrocarbons, preferably of the benzene series, dialkylethers, glycol ethers, (non-polar) alcohols, esters, ketones, solubilising ink vehicle components, monomers (acrylate monomers) and mixtures thereof.
- 7. The composition according to claim 5, wherein the resin acid (3) is an organo-soluble acid selected from the group consisting of rosin acid, abietyl resin, colophony or derivatives thereof, in particular chemically modified rosin acids.
- 8. The composition according to claim 1, which comprises
- 0.1 50 % by weight of component (1),
- 1 95% % by weight of component (2),
- 0.1-75 % of component (3), and
- 0 50 % of component (4).
- 9. The composition according to any one of claims 1 to 8 which additionally comprises an ink vehicle resin or binder.
- 10. The composition according to any one of claims 1 to 9 wherein the organic solvent is a non-polar organic solvent.
- 11. The composition according to any one of claims 1 to 10 wherein the printing ink composition is a gravure printing ink composition.
- 12. A process for the preparation of printing ink compositions according to claim 1 which comprises mixing together

(a) a carbinol dye precursor of the formula (2)

$$(R_6)_n \xrightarrow{R_2} R_3 \\ N \xrightarrow{R_4} (R_5)_m$$
 (2)

or a mixture thereof, dissolved or dispersed in an organic solvent, wherein R_1 - R_6 are independently of one another hydrogen, substituted or unsubstituted alkyl, alkoxy, cycloalkyl, aryl, heteroaryl or allyl, R_2 and R_3 may be combined together to form a ring, further R_5 and R_6 are independently of one another halogen, cyano, nitro, aryloxy, alkenyl, alkenoxy, alkoxcarbonyl, aryloxycarbonyl, acyloxy, acyl, alkylthio, arylthio, acylamino, alkylsulfonyl, arylsulfonyl or thiocyano, any two of R_5 or any two of R_6 may be combined together to a homocyclic or heterocyclic aromatic or non-aromatic ring, A is -OR, $-N(R)_2$, -N(R)COR, $-N(R)SO_2R$, -SR, -S(O)R, $-O_2CR$, $-N(R)CON(R)_2$, $-OCON(R)_2$, $-SO_2N(R)_2$ or -N(R)COOR, wherein R is R_1 , m is an integer of 1 to 5 and n is an integer of 1 to 4, with

- (b) a solution of an organic acid, preferably an organic resin acid, dissolved in an organic solvent, and with
- (c) optionally a pigment.
- 13. The process according to claim 12, wherein R_1 - R_6 in the carbinol dye precursor of formula (2) are independently of one another hydrogen, unsubstituted or substituted alkyl or alkoxy of 1 to 10 carbon atoms, cycloalkyl of 5 to 10 carbon atoms, aryl of 6 to 10 carbon atoms, heteroaryl of 5 to 10 atoms, comprising one or more nitrogen, oxygen or sulfur atoms as ring members, or allyl, R_2 and R_3 may be combined together to form a 5 to 7-membered ring, and A m and n have the meanings indicated.
- 14. A process for the preparation of gravure printing ink compositions according to claim 1 which comprises mixing together
- (a) a carbinol dye precursor of the formula (2)

$$(R_6)_n \xrightarrow{R_2} \begin{array}{c} R_3 \\ N - N \\ R_1 \end{array} \qquad (2)$$

or a mixture thereof, dissolved or dispersed in an organic solvent, wherein R_1 - R_6 are independently of one another hydrogen, substituted or unsubstituted alkyl, alkoxy, cycloalkyl, aryl, heteroaryl or allyl, R_2 and R_3 may be combined together to form a ring, further R_5 and R_6 are independently of one another halogen, cyano, nitro, aryloxy,

alkenyl, alkenoxy, alkoxcarbonyl, aryloxycarbonyl, acyloxy, acyl, alkylthio, arylthio, acylamino, alkylsulfonyl, arylsulfonyl or thiocyano, any two of R_5 or any two of R_6 may be combined together to a homocyclic or heterocyclic aromate or non-aromatic ring, A is -OR, -N(R)COR, $-N(R)SO_2R$, -SR, -S(O)R, $-O_2CR$, $-N(R)CON(R)_2$, $-OCON(R)_2$, -OCO

 $SO_2N(R)_2$ or -N(R)COOR, wherein R is R₁, m is an integer of 1 to 5 and n is an integer of 1 to 4, with

(b) a solution of an organic acid, preferably an organic resin acid, dissolved in an organic solvent,

evaporating off the solvent (under reduced pressure) from that mixture until a dry mixture is obtained, and redissolving the dry mixture in an organic solvent compatible with the printing ink system, and with

- (c) optionally an organic pigment.
- 15. The process according to claim 14, wherein R_1 - R_6 in the carbinol dye precursor of formula (2) are independently of one another hydrogen, unsubstitued or substituted alkyl or alkoxy of 1 to 10 carbon atoms, cycloalkyl of 5 to 10 carbon atoms, aryl of 6 to 10 carbon atoms, heteroaryl of 5 to 10 atoms, comprising one or more nitrogen, oxygen or sulfur atoms as ring members, or allyl, R_2 and R_3 may be combined together to form a 5 to 7-membered ring, and A, m and n have the meanings indicated.
- 16. The process according to claim 15, wherein R_1 - R_4 are methyl, R_5 is methyl or methoxy (m is 1) or two R_5 together form -O-CH₂-O-CH₂-, R_6 is hydrogen, A is -OH and n is 1.

- 17. The process according to claim 12, wherein components (b) and (c) together constitute a resinated pigment.
- 18. The process according to any of claims 12 to 17, wherein the organic solvent for component (b) is a member selected from the group consisting of optionally halogenated aliphatic hydrocarbons, optionally halogenated aromatic hydrocarbons, preferably of the benzene series, dialkylethers, glycol ethers, alcohols, esters, ketones, solubilising ink vehicle components, monomers (acrylate monomers) and mixtures thereof.
- 19. The process according to any one of claims 14 to 16, wherein the organic solvent for component (b) is a member selected from the group consisting of halogenated aliphatic hydrocarbons, dialkylethers and ketones, the organic solvent for the redissolving step a member selected form the group consisting of aromatic hydrocarbons, aliphatic alcohols and esters.
- 20. The process according to claim 14, which additionally comprises mixing an ink vehicle with components (a), (b) and optionally (c).
- 21. The process according to claim 14, which additionally comprises mixing an ink vehicle with the combined dry or redissolved components (a) and (b), and optionally component (c).
- 22. The process for the preparation of printing ink compositions according to claim 1, which comprises dry mixing components (a) with an organic (resin) acid, and optionally with component (c), and then co-dissolving this mixture in an organic solvent.
- 23. The dry mixture of components (a), the organic (resin) acid, and optionally (c), used in the process according to claim 22.
- 24. The co-dissolved mixture of components (a), the organic (resin) acid, and optionally (c) obtained according to claim 22.
- 25. The process according to claim 20, which comprises dry mixing components (a), the organic (resin) acid, and optionally (c), and an ink vehicle, and then co-dissolving this mixture in an organic solvent.

- 26. The dry mixture of components (a), the organic (resin) acid, optionally (c), and an ink vehicle used in the process according to claim 25.
- 27. The co-dissolved mixture of components (a), the organic (resin) acid, optionally (c), and an ink vehicle obtained according to the process of claim 25.
- 28. The process according to claim 20, which comprises incorporating components (a), the organic (resin) acid, and optionally (c) separately or as dry mix into preformed ink vehicles.
- 29. The process according to claim 25, which comprises extruding the components (a), the organic (resin) acid, and optionally (c) separately or as dry mix into high solids dispersions, solutions or pastes of the ink vehicles.
- 30. The extrusion products obtained according to the process of claim 29.
- 31. Use of the composition according to any one of claims 1 to 10 as printing inks.
- 32. Use of the composition according to claim 11 as gravure printing inks.
- 33. Use of the composition according to any one of claims 1 to 11 as toning agents for predominantly pigment based gravure printing inks.
- 34. Process for printing which comprises printing a flat substrate with a printing ink composition according to any one of claims 1 to 10.
- 35. Process for printing which comprises printing a flat substrate with a predominantly pigment based printing ink containing a compositions according to any one of claims 1 to 10 as toning agents.
- 36. Process according to any one of claim 34 or 35 wherein the printing process is a publication or packaging gravure, flexographic, lithographic or letterpress printing process.